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ARTICLE

Lycopene Degradation and Isomerization Kinetics during Thermal Processing of an Olive Oil/Tomato Emulsion

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The stability of lycopene in an olive oil/tomato emulsion during thermal processing (80−140 °C) was studied. Initially, the degradation of total lycopene (*all-E* plus *Z*-forms) occurred quickly at temperatures above 100 °C. However, a nonzero plateau value, depending on the processing temperature, was attained after longer treatment times. Besides degradation, the isomerization of total-*Z*-lycopene as well as the individual isomerization of *all-E*-, 5-*Z*-, 9-*Z*-, and 13-*Z*-lycopene was studied in detail. After prolonged heating, the isomer conversion reached a temperature-dependent equilibrium state. The degradation of total lycopene and the isomerization could be described by a fractional conversion model. The temperature dependency of the corresponding reaction rate constants was quantified by the Arrhenius equation. The activation energy of degradation was estimated to be 28 kJ/mol, and the activation energy of overall (*all-E* and total-*Z*) isomerization was estimated to be 52 kJ/mol.

KEYWORDS: Lycopene; tomato; olive oil; degradation; isomerization; kinetics; thermal processing

INTRODUCTION

Lycopene is a symmetrical, acyclic C_{40}-carotenoid and imparts the red color of fruits and vegetables such as tomato, watermelon, guava, pink grapefruit, papaya, and rosehip (*1*). Chemically, lycopene consists of 13 double bonds, of which 11 are conjugated. In plant sources, lycopene primarily exists in the *all-E* form, but in principle, 1056 geometrical isomers of lycopene are possible, of which 72 are not sterically hindered (*2*). Several epidemiological studies suggest an inverse relationship between lycopene-rich diets and the risk of chronic diseases (*3*, *4*). Due to its system of conjugated double bonds, lycopene is a carotenoid with an effective antioxidant activity (*5*, *6*). This antioxidant property is thought to be primarily responsible for the beneficial effects of lycopene on human health. Compared to *all-E*-lycopene, higher antioxidant activity is attributed to its *Z*-isomers (*7*). Moreover, *Z*-lycopene isomers have been found to be more bioavailable (*8*).

Tomatoes are considered to be the most important dietary source of lycopene. Consumers' demand for convenience food products is still growing. As a consequence, tomatoes are often processed into products that contain vegetable oil such as sauces, juices, and soups or used as an ingredient of fully prepared meals. During thermal processing, lycopene can undergo changes due to isomerization from *all-E* to mono-*Z* and poly-*Z* forms or due to degradation via oxidation. Lycopene stability has previously been studied in different model systems and tomato-based matrices (*9*). The data in the literature generally agree that lycopene is quite stable in tomato matrices during mild thermal treatments, but during intense processing conditions or when lycopene is dissolved in oil or in organic solvent, degradation and isomerization might occur rapidly (*10*). Lycopene degradation during thermal processing has previously been described by a first-order kinetic model in organic solvents (*11*), in oil-in-water emulsions (*12*), in safflower oil (*13*), and in plain tomato puree (*14*, *15*). Furthermore, lycopene degradation has been described by a fractional conversion model in tomato peel (*16*). In the literature, kinetic data describing the effect of thermal treatments on the lycopene isomerization are limited. Ax et al. (*12*) studied the changes in the *all-E*-, 9-*Z*-, and 13-*Z*-lycopene content during incubation of an oil-in-water emulsion at 90 °C during 7 h. They reported a significant decrease of *all-E*- and 13-*Z*-lycopene accompanied by an increase of 9-*Z*-lycopene. Shi et al. (*14*) subjected plain tomato puree to intensive heat treatments (90−150 °C for 1−6 h). Their results showed an increase in the *Z*-lycopene isomer level only during the first 1−2 h.

The objective of this study was to investigate the effect of thermal processing on lycopene stability in an olive oil/tomato emulsion using a kinetic approach. Knowledge on the kinetic models and associated parameters of lycopene degradation and isomerization reactions would provide a useful tool for process design and optimization. Insight into degradation and isomerization of lycopene in an olive oil/tomato emulsion may better relate to real lipid-containing food systems than the lycopene changes studied in model systems or plain tomato puree.

MATERIALS AND METHODS

Materials. Mature red ripe tomatoes (*Lycopersicon esculentum* var. Heinz 9997) were harvested in Spain in 2009. The tomatoes were washed, quartered, frozen in liquid nitrogen, and stored at −40 °C. Before use, the frozen tomato quarters were thawed, mixed (three times for 5 s) (Büchi Mixer

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B-400, Flawil, Switzerland), and sieved (pore size = 1.0 mm) to obtain a tomato pulp free from skin and seeds. Extra virgin olive oil (5% w/w) (degree of saturation = 15%, poly unsaturated lipids = 8%) was added to the tomato pulp, and the mixture was high-pressure homogenized at 100 bar (Panda 2K, Gea Niro Soavi, Mechelen, Belgium) to obtain a stable emulsion.

Lycopene isomer standards were purchased from CaroteNature (Lupsingen, Switzerland), and β-apo-8′-carotenal was obtained from Sigma-Aldrich (Belgium). All chemicals and reagents used were of analytical or HPLC grade.

Experimental Setup. All heat treatments were performed in closed reactor tubes (external diameter = 12 mm, internal diameter = 9 mm, length = 100 mm). To minimize the contact with oxygen, the reactor tubes were filled completely with the prepared oil/tomato emulsion so that the headspace was negligible. The filled reactor tubes were equilibrated during 20 min at 40 °C to reduce the dynamic heating phase during the actual thermal treatment. The actual heat treatment was performed by immersing the tubes into an oil bath at a preset temperature during preset time intervals. Immediately after the treatment, the samples were cooled in ice−water to stop any further reaction, removed from the reactor tubes, vacuum-packed in plastic pouches, frozen in liquid nitrogen, and stored at −80 °C until lycopene isomer analysis. During the thermal treatments, the time/temperature profiles of the oil/tomato emulsion were registered using an Ellab E-val data-acquisition system (TM 9616, Ellab, Hilleroed, Denmark) and thermocouples (type T, Thermo Electric Benelux, Balen, Belgium).

Lycopene Isomer Analysis. The lycopene extraction procedure was based on the method of Sadler et al. (*17*). Concisely, 2.0 g of the oil/tomato emulsion was stirred with 0.5 g of NaCl and 50 mL of hexane/acetone/ethanol (50:25:25) containing 0.1% butylated hydroxytoluene during 20 min at 4 °C. Reagent grade water (15 mL) was added and stirred for an additional 10 min. The apolar phase, containing carotenoids, was collected and filtered (Chromafil PET filters, 0.20 μm pore size, 25 mm diameter), and 5.0 mL was dried under vacuum using a rotary evaporator at 30 °C until semidry. The concentrated lycopene was redissolved in 400 μL of hexane/dichloromethane (4:1) and transferred to an amber HPLC vial. The concentration factor was calculated by adding a known amount of β-apo-8′-carotenal prior to the evaporation of the apolar solvent. For each sample, the extraction of lycopene was performed at least in duplicate.

An HPLC system (Agilent Technolgies 1200 series, Diegem, Belgium), equipped with a reversed phase C_{30} column (3 μm × 150 mm × 4.6 mm, YMC Europe, Dinslaken, Germany) coupled to a guard column (3 μm × 10 mm × 4.0 mm, YMC Europe) was used to separate different lycopene isomers. The columns were held at 25 °C. The separation was carried out by gradient elution with reagent grade water (A), methanol (B), and methyl *tert*-butyl ether (C) at a flow rate of 1 mL/min. The following gradient program was used: linear change from 4% of A, 81% of B, and 15% of C to 4% of A, 36% of B, and 60% of C during 5 min followed by the linear change to 4% of A, 28% of B, and 68% of C during another 25 min. Next, the column was washed with 4% of A, 16% of B, and 80% of C during 5 min and equilibrated again at the starting conditions. Lycopene isomers were detected using a diode array detector. Analyses were performed under dim light to prevent sample degradation by photo-oxidation.

Lycopene Isomer Identification and Quantification. Lycopene isomers were identified on the basis of retention times and spectral characteristics (see the Supporting Information). In addition, RP-HPLC-MS measurements were performed to confirm the mass of the lycopene isomers. The mass spectrum was monitored in the mass range m/z 200−1000 on an LCQ ion trap triple-quadrupole mass spectrometer (Finnigan, Thermo Electron Corp., Boston, MA) equipped with an APCI interface and operated in the positive mode. The capillary and vaporizer temperatures were set at 200 and 450 °C. The corona discharge current was 5 μA, and the sheath gas flow was held at 80 mL/min. All lycopene isomers showed spectra with strong mass signals at m/z 537, corresponding to the quasimolecular ion of lycopene, which excluded their identification as oxidized products. Because only external standards are commercially available for *all-E*- and 5-*Z*-lycopene, only these two isomers could be fully identified. Two peaks were tentatively identified as 13-*Z*- and 9-*Z*-lycopene by comparing their spectral characteristics (see the Supporting Information) with data reported in the literature (*18*, *19*).

all-E-Lycopene and 5-*Z*-lycopene were quantified with the aid of their corresponding calibration curves. Other *Z*-isomers were quantified using the calibration curve of *all-E*-lycopene. The wavelength for quantification was 472 nm, at which maximal absorbance of *all-E*-lycopene was found. The total lycopene content was calculated as the sum of the content of all lycopene isomers observed in the HPLC chromatogram, whereas the total-*Z*-lycopene content is the sum of the content of all *Z*-lycopene isomers present.

Kinetic Modeling. Kinetic parameters of lycopene degradation and isomerization reactions were estimated with the aid of both two-step and one-step nonlinear regression analysis. As mentioned before, first-order kinetic models have been reported to describe lycopene changes in oil-containing model systems (*12*, *13*) and in plain tomato matrices (*14*, *15*), whereas a fractional conversion model was applied to describe lycopene degradation in tomato peel (*16*). In the current study, a nonzero plateau value of the reactants was obtained after long reaction times (up to 60 min). Therefore, a fractional conversion model was used to describe the time-dependent lycopene changes. This model differs from a first-order reaction model only in the fact that a nonzero equilibrium value is considered at infinite time. The fractional conversion model can be written as

$$\frac{dC}{dt} = -k(C - C_f) \tag{1}$$

or in integrated form as

$$C = C_f + (C_0 - C_f)\exp(-kt) \tag{2}$$

where C is the lycopene isomer content, C_f the lycopene isomer content in equilibrium state, C_0 the initial lycopene isomer content, k the reaction rate constant (min^{-1}), and t the reaction time (min).

The effect of temperature on lycopene degradation and isomerization was expressed by the Arrhenius equation, in which the temperature dependency of the rate constant k is quantified by the activation energy (E_a) (J/mol) according to

$$k = k_{ref}\exp\left[\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \tag{3}$$

where R represents the universal gas constant (8.314 J/mol K), T the temperature concerned, and k_{ref} the reaction rate constant at a reference temperature (T_{ref}) of 110 °C.

To obtain the kinetic parameter estimates, first, a two-step regression method was applied assuming isothermal conditions. Herein, the C_f values were estimated for each treatment temperature from eq 2. Next, one-step regression analysis, taking into account the actual nonisothermal conditions, was applied. In this approach, rate constants and activation energies are estimated simultaneously from the data at different temperatures. Hereto, the Arrhenius equation (eq 3) is substituted in the fractional conversion model (eq 1) and the experimental temperature history of each sample was included by using the equation

$$dC = -(C - C_{f(T)})k_{ref}\exp\left[\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T_{(t)}}\right)\right]dt \tag{4}$$

where $C_{f(T)}$ represents the temperature-dependent lycopene content in equilibrium. The $C_{f(T)}$ values were fixed at the values estimated by two-step regression analysis under isothermal conditions. For the one-step regression analysis, the dynamic time/temperature profiles were considered instead of isothermal conditions, because of improved accuracy of the prediction.

The kinetic parameters were estimated by minimizing the sum of squares of errors by nonlinear regression (statistical software package SAS, version 9.2, Cary, NC). The model quality was evaluated by visual inspection of residual plots, by the correlation coefficient between the predicted and the observed values (parity plot), and by checking if the intercept and the slope of the linear regression line approached, respectively, 0 and 1.

RESULTS AND DISCUSSION

First, to determine the relevant treatment conditions for the actual kinetic study, a screening study was performed. Therefore, the oil/tomato emulsion, enclosed in the reactor tubes, was

treated during 30 min at temperatures ranging from 60 to 140 °C. Analysis of the lycopene isomer content revealed that the lycopene degradation and isomerization at 60 and 70 °C were limited. Therefore, the interesting temperature range to study lycopene degradation and isomerization kinetics was 80−140 °C (data not shown). This temperature range was used for the kinetic experiments.

Total Lycopene Degradation. The total lycopene content obtained after heating during 0−60 min at temperatures between 100 and 140 °C is expressed relative to the total lycopene content of the untreated sample and is represented in **Figure 1** as single data points. Temperatures below 100 °C hardly caused degradation during the time period studied. At temperatures above 100 °C, the total lycopene degradation generally increased with treatment temperature. Moreover, for each temperature, a different plateau value was attained after extended treatment times. The fact that lycopene was not completely broken down after prolonged heating might be partly explained by the consumption of the oxygen present in the closed reactor tubes, which stopped the oxidative degradation of lycopene. Moreover, it could be partly due to the time-dependent regeneration of oxidized lycopene by ascorbic acid present in the tomato matrix, as was found by Biacs and Daood (*20*).

One-step regression analysis, taking into account the actual nonisothermal conditions and using a fractional conversion model, was applied to estimate the kinetic parameters according to eq 4. The $C_{f(T)}$ values were fixed at the values estimated by two-step regression analysis under isothermal conditions, which are given in **Table 1**. The predicted lycopene contents are shown in **Figure 1** by the full lines. The estimated kinetic parameters are reported in **Table 2**. The activation energy for total lycopene degradation was 28 kJ/mol. This value agrees with corresponding values reported for total lycopene degradation in an oil-in-water emulsion in oxygen-saturated conditions (18 kJ/mol) and in oxygen-free conditions (23 kJ/mol) (*12*). Furthermore, the activation energy obtained in the current study is of the same order of magnitude as the activation energy reported for lycopene degradation in tomato peel (18 kJ/mol) (*16*). Higher activation energies of 61 and 83 kJ/mol have been found for the degradation of a lycopene standard dissolved in, respectively, hexane and safflower oil (*11*, *13*). Differences in degradation activation energies might be caused by the presence of different compounds, such as antioxidants and differences in sample matrices.

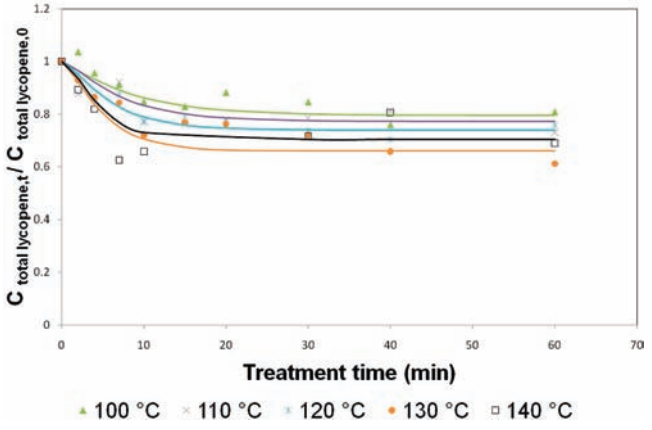

Figure 1. Relative total lycopene content after thermal treatments of oil/tomato emulsions modeled by one-step regression using a fractional conversion model. The experimental values are represented by single data points, whereas the full lines represent the values predicted by the model.

Visually, it can be observed from **Figure 1** that the proposed model could not fully explain the experimental data. Also, the R^2 of the parity plot somewhat deviated from 1. The difference between the experimental and predicted values might be caused by several factors. The lycopene isomer content, which is measured after a thermal treatment of a tomato matrix, is influenced by degradation and isomerization but also by the extraction efficiency from the matrix. Tomato processing involves changes in the structural integrity of the matrix, which could result in a higher extractability of lycopene. However, the enhanced extractability might be counterbalanced by a more pronounced lycopene degradation. Although varying extractability has been reported previously (*21*−*23*), no clear relationship has been described between lycopene extractability and processing conditions.

Lycopene Isomerization. To rule out the problem of changing lycopene extractability as a function of treatment time and temperature, the data were transformed as suggested by Lemmens et al. (*24*). For each time/temperature combination, the contribution of each isomer to the total lycopene content was calculated as follows:

$$\frac{C_{\text{lycopene isomer},t}}{C_{\text{total lycopene},t}} 100\% \quad (5)$$

In this way the extraction yield is canceled out, assuming that for a given sample the extractability of each lycopene isomer is the same. Moreover, it is assumed that the isomerization products are limited to the lycopene isomers observed on the HPLC chromatogram. This assumption is reasonable because all peaks with a m/z value of 537 were taken into account. Moreover, in the literature, it is reported that *all-E*-lycopene is quantitatively the most important isomer in tomato matrices and among the *Z*-isomers, 5-*Z*-, 9-*Z*-, and 13-*Z*-lycopene usually predominate (*19*).

The transformed data represent the net isomerization and were used for further data analysis on lycopene isomerization kinetics.

The isomerization of total-*Z*-lycopene was studied as well as the individual isomerization of *all-E*-, 5-*Z*-, 9-*Z*-, and 13-*Z*-lycopene. In **Figures 2** and **3** the experimental isomer contributions are expressed relative to the initial isomer contribution and are shown by single data points. At low treatment temperatures

Table 1. Absolute Total Lycopene Content in Equilibrium State ($C_{f(T)}$) (μg/g FW) and Contribution of Different Lycopene Isomers in Equilibrium State ($C_{f(T)}$) (%) ± Standard Error Estimated by Two-Step Regression Analysis Using a Fractional Conversion Model

T (°C)	total (μg/g FW)	*all-E* (%)	total-*Z* (%)	5-*Z* (%)	9-*Z* (%)	13-*Z* (%)
80	ne[a]	71.5 ± 3.6	28.5 ± 3.6	ne	ne	8.63 ± 0.84
90	ne	76.3 ± 1.4	23.7 ± 1.4	ne	ne	7.93 ± 0.60
100	60.7 ± 2.4	68.4 ± 1.7	31.6 ± 1.7	5.90 ± 0.11	ne	9.56 ± 0.60
110	55.0 ± 1.6	63.0 ± 1.1	37.0 ± 1.1	2.82 ± 2.6	23.3 ± 9.7	10.2 ± 0.44
120	45.7 ± 1.0	50.3 ± 1.0	49.7 ± 1.0	3.69 ± 0.16	20.8 ± 1.7	11.8 ± 0.64
130	41.1 ± 1.7	51.4 ± 0.98	48.6 ± 0.98	2.93 ± 0.31	20.0 ± 1.3	9.90 ± 0.45
140	43.3 ± 2.2	44.8 ± 1.2	55.2 ± 1.2	2.44 ± 0.17	21.3 ± 1.5	11.6 ± 0.27

[a] ne, not estimated.

Table 2. Kinetic Parameters ± Standard Error for the Degradation and Isomerization of Different Lycopene Isomers Estimated by One-Step Regression Analysis Using a Fractional Conversion Model

	T range (°C)	E_a (kJ/mol)	k_{ref} (min^{-1})	R^2 parity plot
degradation of total	100−140	28.1 ± 8.8	0.15 ± 0.02	0.79
isomerization of *all-E*	80−140	52.1 ± 4.3	0.11 ± 0.01	0.98
formation of total-*Z*	80−140	52.1 ± 4.3	0.11 ± 0.01	0.98
isomerization of 5-*Z*	100−140	31.3 ± 6.7	0.077 ± 0.01	0.95
formation of 9-*Z*	110−140	157 ± 6.2	0.017 ± 0.001	0.99
formation of 13-*Z*	80−140	132 ± 10	1.56 ± 0.3	0.95

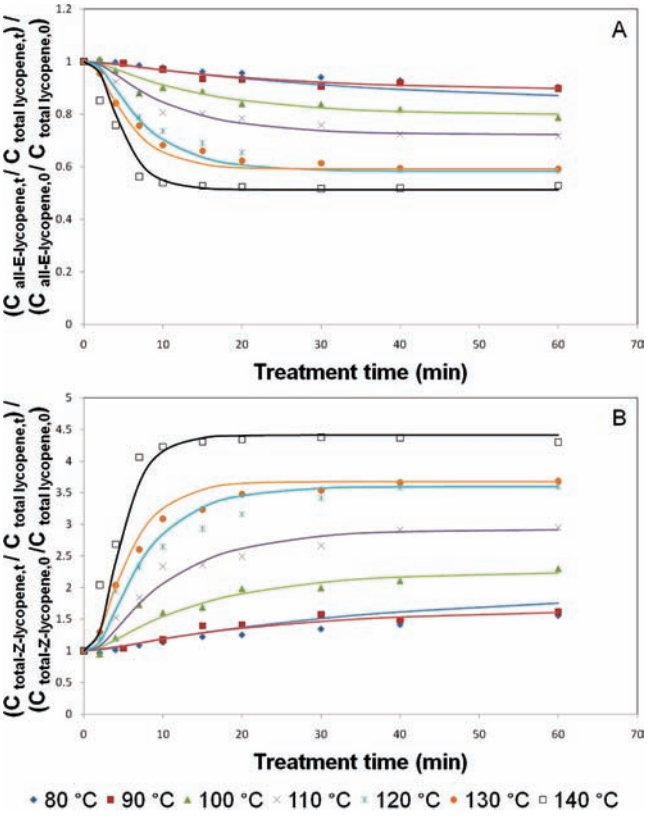

Figure 2. Isomerization of *all-E*-lycopene (**A**) and isomerization into total-*Z*-lycopene (**B**) during thermal treatments of oil/tomato emulsions modeled by one-step regression using a fractional conversion model. The experimental values are represented by single data points, whereas the full lines represent the values predicted by the model.

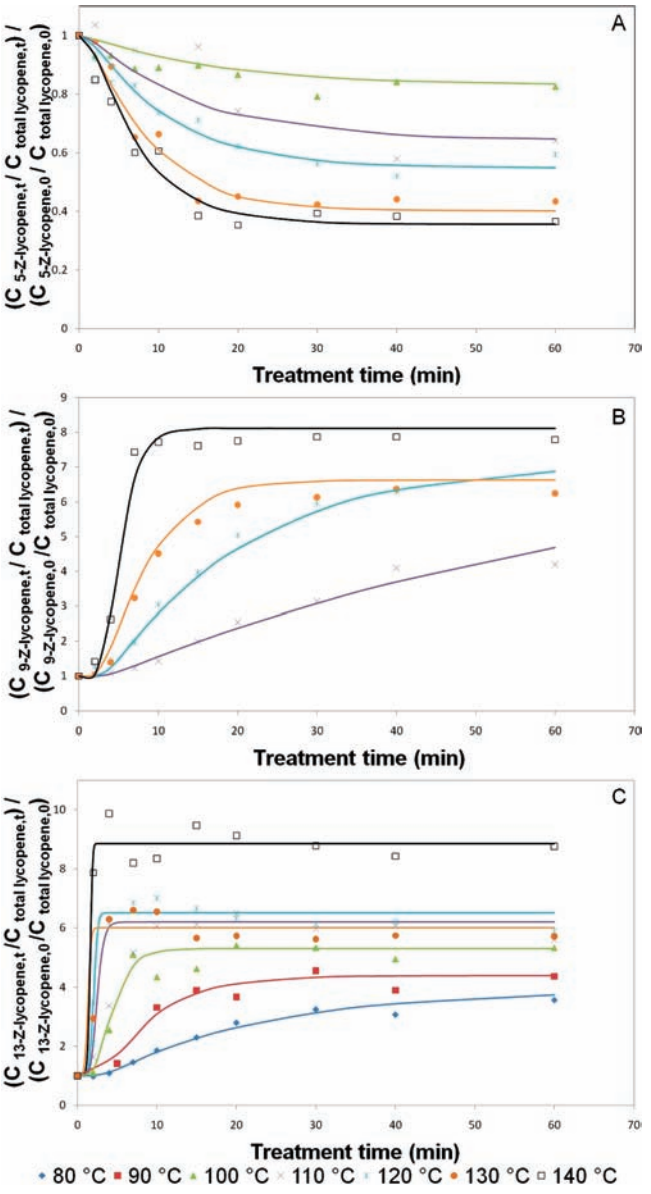

Figure 3. Isomerization of 5-*Z*-lycopene (**A**), isomerization into 9-*Z*-lycopene (**B**), and isomerization into 13-**Z**-lycopene (**C**) during thermal treatments of oil/tomato emulsions modeled by one-step regression using a fractional conversion model. The experimental values are represented by single data points, whereas the full lines represent the values predicted by the model.

(80−90 °C), isomerization of *all-E*-lycopene and total-*Z*-lycopene hardly occurred, and the isomerization rate did not significantly increase by increasing the treatment temperature from 80 to 90 °C (**Figure 2**). The results showed only minor changes in the contribution of 5-*Z*-lycopene and 9-*Z*-lycopene below treatment temperatures of, respectively, 100 and 110 °C (data not shown). In addition, it was observed that, during thermal treatment, the contribution of *all-E*- and 5-*Z*-lycopene decreased, whereas other *Z*-lycopene isomers were formed. The deviating behavior of 5-*Z*-lycopene compared to other *Z*-isomers might be explained by the considerably larger rotational barrier for the conversion of *all-E*- to 5-*Z*-lycopene than to other mono-*Z*-isomers (*25*). After a certain treatment time, the contribution of the different isomers evolved to a plateau value, implying that an equilibrium state is attained.

Also in this analysis, the one-step regression approach was applied, assuming a fractional conversion model and taking into account the dynamic heating conditions. Hereto, the kinetic parameters were estimated using eq 4. The fixed $C_{f(T)}$ values, which were estimated by two-step regression analysis under isothermal conditions, are given in **Table 1**. The $C_{f(T)}$ values obtained for the total-*Z*-lycopene contributions at temperatures above 110 °C were between 50 and 55%. This contribution of *Z*-lycopene is in close agreement with the data of Unlu et al. (*26*). These authors obtained 45% *Z*-isomers of total lycopene after treating a tomato juice with 10% maize oil for 40 min at 127 °C in a steriotort. Moreover, it has been suggested that, at the thermodynamic equilibrium, lycopene exists as a 50:50 mixture of *all-E*- and *Z*-lycopene (*27*).

In the case of β-carotene in carrot puree, carotenoid isomerization was also modeled by a fractional conversion model. Moreover, for *Z*-isomers of β-carotene, a linear increase of $C_{f(T)}$ with treatment temperature was reported (*24*). In the current study, such correlation was not observed for lycopene isomerization.

In **Figure 2**, the predicted isomerization of *all-E*-lycopene and the predicted isomerization into total-*Z*-lycopene is represented by the full lines. It can be visually observed that the proposed

models describe the experimental data well. Moreover, a good correlation was found between the experimental and predicted isomer contributions (R^2 parity plot = 0.98). The model parameters are listed in **Table 2**. Because data are expressed as contributions of total lycopene, equal activation energies and k_{ref} values were expected for isomerization of *all-E*-lycopene and formation of total-*Z*-lycopene. The activation energy of 52 kJ/mol obtained in the current study was considerably larger than the activation energy of 4 kJ/mol found for the *E*/*Z* isomerization during thermal processing of plain tomato puree (*14*). This difference might be attributed to the presence of olive oil, in which lycopene crystals can dissolve, in the samples used in the current study.

To study the lycopene isomerization more into detail, the isomerization of 5-*Z*-lycopene and the formation of 9-*Z*- and 13-*Z*-lycopene were modeled individually. The proposed models and the corresponding experimental data are shown in **Figure 3**. As mentioned above, almost no isomerization of 5-*Z*-lycopene occurred below 100 °C. Therefore, only temperatures starting from 110 °C were included in the model. Furthermore, because no formation of 9-*Z*-lycopene was observed at temperatures below 110 °C, only data between 120 and 140 °C were used to determine the kinetic model that is suitable to describe its formation. The goodness of the model fits is confirmed by the high correlation coefficients of the corresponding parity plots (**Table 2**). **Table 2** summarizes all model parameters obtained for the different lycopene isomers. The activation energies for 5-*Z*, total-*Z*, and *all-E* are significantly lower compared to the activation energies for 9-*Z* and 13-*Z*. In addition, the k_{ref} value for 13-*Z* was significantly higher than that for 9-*Z*-lycopene, which can also be seen from **Figure 3**. However, the estimated temperature sensitivity of the rate constants for 9-*Z*- was significantly higher than that for 13-*Z*-lycopene. This could be explained by the fact that the rotational barrier for conversion of *all-E*- to 13-*Z*-lycopene is smaller than that for the conversion to 9-*Z*-lycopene (*25*).

Upon treatment at temperatures above 110 °C, 13-*Z*-lycopene reached almost immediately its maximal value. From the experimental values, it even seems that, after a treatment of 10 min at such high temperatures, the contribution of 13-*Z*-lycopene starts to decrease slightly. Previously, Lambelet et al. (*28*) heated (76 °C) a raw tomato extract in ethyl acetate up to 168 h. On the one hand, they observed that a considerable amount of 13-*Z*-lycopene was formed at an early stage (up to 2 h), whereafter its proportion decreased over time. On the other hand, the fraction of the 9-*Z*-isomer increased rapidly within the first 48 h and then slightly diminished over the next 120 h. Contrarily, in the current study, a decrease in the proportion of 9-*Z*-lycopene was not found within the time frame studied. This might be due to the fact that 9-*Z*-lycopene is more thermostable than 13-*Z*-lycopene (*25*, *29*). Moreover, the 9-*Z*-isomer has a larger rotational barrier compared to 13-*Z* for the retro-isomerization to *all-E* (*25*). Previously, Shi et al. (*14*) reported that the *Z*-isomer level increased only during the first 1−2 h of heating plain tomato puree at temperatures between 90 and 150 °C, whereas for the remaining heating time (up to 6 h), the *Z*-isomer level decreased. Furthermore, **Figure 3C** shows that the formation of 13-*Z*-lycopene at 130 °C evolved to a $C_{f(T)}$, which was unexpectedly lower than the $C_{f(T)}$ value at 110 and 120 °C. The results of the current study indicate that interconversions of 13-*Z*-lycopene might occur at high temperatures, which are not yet fully understood and which might be better explained by a more complex kinetic model.

In general, it can be stated that a fractional conversion model was suitable to describe the total lycopene degradation and isomerization during thermal processing of an oil/tomato emulsion between 80 and 140 °C. From an industrial point of view, the kinetic data might be of great interest for process design and optimization purposes. Using the model and its associated parameters, the impact of different processing scenarios (dynamic time/temperature profiles) on lycopene degradation and isomerization in an olive oil/tomato emulsion system can be evaluated. It is believed that *Z*-isomers of lycopene have additional health-promoting effects compared to *all-E*-lycopene because they are more bioavailable (*8*) and possess a higher antioxidant activity (*7*). Hence, the proposed kinetic models can be applied to minimize total lycopene loss and maximize the total-*Z* contribution. The time/temperature range investigated in the current study covers both the pasteurization and sterilization ranges. Next to the pasteurization range, the information on sterilization might be valuable for processing of tomato-based sauces or fully prepared meals that have a pH value above 4.6.

Supporting Information Available: Retention times of the different lycopene isomers accompanied by their spectral characteristic. This material is available free of charge via the Internet at http://pubs.acs.org.

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